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Graphical Abstract
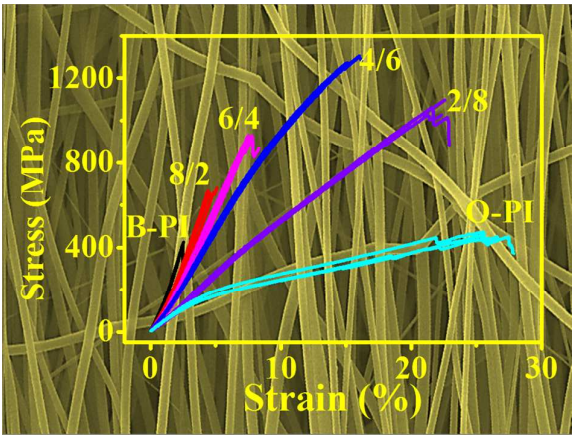
Aligned electrospun PI nanofibers with excellent mechanical properties were prepared by electrospinning the blend-PAA solutions followed with thermal imidization.

Journal Name

ARTICLE

Highly Strong and Highly Tough Electrospun Polyimide/Polyimide Composite Nanofibers from Binary Blend of Polyamic Acids

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Electrospun blend-polyimide (blend-PI) nanofibers with high tensile strength and toughness were highlighted in this article. The blend-PI nanofibers were prepared by electrospinning the binary blend of rigid and flexible polyamic acids followed with thermal imidization. The method is simple and can be extended to the other kinds of polyamic acids. The morphologies and structures of the blend-PI nanofibers were investigated by scanning electron microscope (SEM) and wide-angle X-ray diffraction (XRD). The mechanical properties, thermal properties and miscibility of the blend-PI nanofibers were studied by tensile test, thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA). The mechanical properties of the blend-PI nanofibers, including tensile strength, modulus, elongation at break and toughness could be well-tuned by modifying the molar ratio of the rigid component (B-PI) and the flexible component (O-PI). The blend-PI nanofibers with B-PI/O-PI molar ratio of 4/6 had the ultra-high strength of 1.3 GPa and excellent toughness of 82 J/g. All the blend-PI nanofibers showed thermal stability of over 500 °C. The only one glass transition temperature (T_g) suggested the good miscibility of the binary PIs in the blend-PI nanofibers. This study would open completely new opportunities for modifying the properties of electrospun PI nanofibers.

1. Introduction

Polyimide (PI) is a promising class of high performance polymers with excellent thermal stability and mechanical properties, outstanding chemical and radiant resistance, long-term stability and superior electrical properties and has been broadly applied in composites, coatings, adhesives, filtrations, insulators and dielectrics in the forms of fibers, films and particles.[1-6]. The fibers or electrospun nanofibers based on the polyimides have high performances and are highly desired in protective clothes, filtration, gas separation, battery separator, composites and so on.[5, 7-11] Conventional as-spun PI fibers showed tensile strength in the range from 0.22 to 0.74 GPa and fibers treated by hot-stretching in the range from 0.8 to 2.7 GPa.[12] The Russian scientists reported the as-spun polyimide fibers with ultra-high ultimate tensile strength of 2.9-3.3 GPa, which is the strongest tensile strength of PI fibers reported up to now.[13, 14] Their studies revealed that the fibers made from co-PI mostly had a much higher tensile strength than those made from the corresponding homo-PI.

In the past decades, our group paid much attention on improving the mechanical properties of electrospun nanofibers.[9,15-19] We found that the electrospun nanofibers made of polyimides had excellent mechanical properties.[18-20] The aligned electrospun PI nanofiber membranes made of rigid 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA)/p-phenylene diamine (PDA) homo-polyimide had an ultra-high tensile strength and modulus;[20] the aligned nanofiber membranes made of a flexible 2,2-bis[(4-(4-amino-phenoxy) phenyl)] hexafluoropropane (6F-BAPP)/BPDA homo-polyimide had a high toughness;[18] and the aligned electrospun co-polyimide nanofiber membranes based on BPDA/4,4′-oxydianiline (ODA) and 4,4′-diaminobiphenyl (BPA) were the strongest aligned electrospun polymer nanofiber membrane reported up to now in our world, which displayed a tensile strength of 1.1 GPa,[19] doubled that of the homo-PI BPDA/BPA and homo-PI BPDA/PDA.

Although co-polymerization gives a better improvement on the fiber mechanical properties, the chemical structures by copolymerization are random and unfixed, which led to an uncertain of the resulting mechanical properties. Nevertheless, the polymer blends have long since been recognized as an efficient method of improving the mechanical properties.[21, 22] Compared with the development of entirely new polyimide and co-polyimide, blending existing polyimides is a simple, economic and low-cost process. Yokota and many other

researchers have shown that the mechanical properties of blend-polyimide were not only higher than those of the corresponding homo-polyimide but also higher than those of the corresponding co-polyimide.[8,23-25]

In order to obtain higher performance electrospun polymer nanofibers with fixed chemical structures by a simple and low-cost process, in this study, a series of blend-polyimide nanofiber membranes (polyimide/polyimide composite nanofibers) with different molar ratios of rigid BPDA/BPA polyimide (B-PI) and flexible BPDA/ODA polyimide (O-PI) were prepared using electrospinning techniques; and the morphology, thermal and mechanical properties of the as-prepared electrospun blend-PI nanofibers were studied in details. The results demonstrated that the electrospun blend-polyimide nanofibers had much better enhanced mechanical and thermal properties depending on the blending ratio of the rigid and flexible polyimides by molar.

2. Experimental

2.1. Materials

3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) (Hebei Jida Plastic Products Co.), 4,4′-diaminobiphenyl (BPA, Quzhou Kaiyuan Fine Chem. Co) and 4,4′-oxydianiline (ODA, Quzhou Kaiyuan Fine Chem. Co) were purified by sublimation in prior to use. N,N-dimethylacetamide (DMAc) (99%, Tianjin Fu Chen Chemical Reagent Factory) was use as received.

2.2. Synthesis of PAA and blending of PAA precursors

The precursors of polyimide, polyamic acids (PAAs) of BPDA/ODA (O-PAA) and BPDA/BPA (B-PAA) were prior synthesized from dianhydride BPDA with two diamines (ODA and BPA) respectively. The polycondensation was performed in DMAc at -5~0 °C for 24 h and the solid contents of PAA solutions were all maintained to 10 wt%. The intrinsic viscosities of B-PAA and O-PAA were 5.2 dL/g and 5.8 dL/g respectively. Different molar ratios of O-PAA and B-PAA in the blend-PAA solutions were prepared via adjusting the weight of O-PAA and B-PAA solutions. The molar ratios of O-PAA and B-PAA were fixed from 0/10, 1/9, 2/8, 3/7, 4/6, 6/4, 7/3, 8/2, 9/1 to 10/0. The molar ratios of O-PAA and B-PAA were calculated according to the equation as following:

$$R = \frac{\dfrac{m_O \times C_O}{M_O}}{\dfrac{m_B \times C_B}{M_B}} = \frac{m_O \times C_O \times M_B}{m_B \times C_B \times M_O}$$

Where R is the molar ratio of O-PAA to B-PAA, m_O, C_O and M_O are the weight of O-PAA solution, the concentration (wt%) of O-PAA solution and the molar mass of the repeating unit of O-PAA; while m_B, C_B and M_B are the weight of B-PAA solution, the concentration (wt%) of B-PAA solution and the molar mass of the repeating unit of B-PAA. Because the repeating unit of O-PAA derived from one molecule of BPDA/ODA and the repeating unit of B-PAA from one molecule of BPDA/BPA, the molar ratios of O-PAA/B-PAA are equivalence with the molar ratios of ODA/BPA and the molar ratios of O-PI/B-PI.

2.3. Preparation of aligned electrospun PI nanofiber membranes

The precursor (polyamic acid) nanofiber membranes were produced by electrospinning the above blending polymer solutions. The absolute viscosity of the solutions was adjusted to about 6 Pa.s in DMAc and the electrical conductivity was about 40 μS/m by adding 0.2 wt% dodecylethyldimethylammonium bromide (DEDAB). The

electrospinning process was performed by applying a positive voltage (15 kV) to the spinneret, and a negative voltage (-5 kV) to the collector. The collecting distance of the spinneret to collector was 25 cm. The feeding rate of the solution was 0.8 mL/h controlled by a digital syringe pump. The laboratory-built rotating disc was used as the collector, which rotated at a surface linear speed of 24 m/s. All the blend-PAA nanofiber membranes were dried at 60 °C in vacuum oven for 4 h to remove the residual solvent, and then thermally imidized in a high-temperature furnace under N_2 atmosphere. The imidization process was performed using the following protocol: (1) quickly heating up to 250 °C at a rate of 10 °C/min and annealing for 30 min; (2) slowly heating up to 370 °C at a rate of 2 °C/min, and annealing at 370 °C for 60 min to finish the imidization. The preparation of co-polyimide was similar to that blend polyimide,[19] and the specific schematic diagrams of blend-polyimide and co-polyimide are shown in **Fig. 1**.
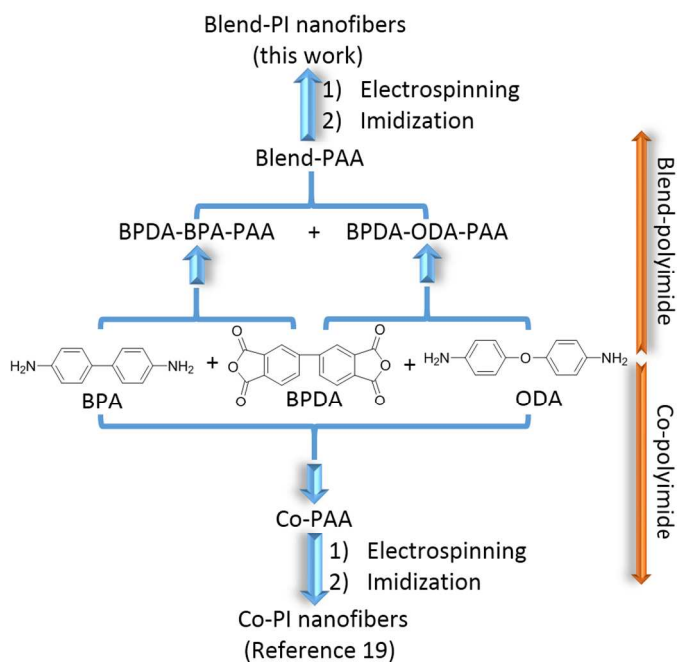

Figure 1. Specific schematic diagrams of Blend-PI and Co-PI.

2.4. Characterizations

A scanning electron microscope (SEM, FEI Quanta 200 FEG) was used to observe the blend-PI nanofiber membranes. Mechanical properties of blend-PI nanofiber membranes were carried out on a computer-controlled electromechanical universal testing machine (SANS, CMT 8102, Shenzhen, China) at a tensile speed of 5 mm/min. The thickness of the samples were calculated similarly to our previously reports.[19] The density (ρ) of PI was calculated from the weight (m) and the volume (V) of the PI films. Thermogravimetric analysis (TGA) was used to explore the thermal stability of the nanofiber membranes under nitrogen atmosphere at a heating rate of 10 °C/min. The dynamic mechanical analysis (DMA) of the samples were performed on a Perkin-Elmer diamond analyzer in tensile mode under nitrogen atmosphere at a heating rate of 3 °C/min in the range of 30 °C to 450 °C. The load frequency and amplitude were 1 Hz and 20 μm, respectively. The X-ray Diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer of crystal monochromated Cu Kα radiation with the

2θ angles ranging from 5° to 40° at 40 kV operating voltage and 20 mA current.

3. Results and discussion

3.1. Morphology of polyimide nanofibers

The morphology of the nanofibers is very important for the mechanical performance of nanofiber belts. The beads or drawbacks on the nanofibers would greatly decrease the mechanical properties.[26] In order to study the blend effect on the mechanical properties of the blend-PI, it is necessary to prepare all the nanofibers homogeneously without beads and other drawbacks. **Fig. 2** showed the morphologies of the aligned homo- and blend-PI nanofibers in this study. The electrospun nanofibers were aligned in the membranes with diameters in the range of 200-300 nm. No beads and/or beaded nanofibers were found by the SEM images. No significant morphological differences were observed between the homo PI (B-PI and O-PI) and blend-PI nanofibers.
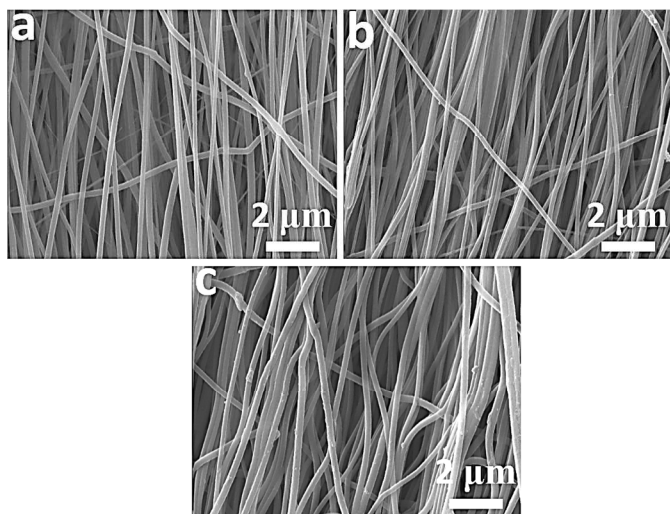
Figure 2. SEM images of the aligned nanofibers of (a) B-PI, (b) O-PI and (c) blend-PI with B-PI/O-PI molar ratio of 4/6.

3.2. Mechanical properties of blend-PI nanofiber membranes

Depending on the molecular structures, electrospun polyimide nanofibers not only have a high tensile strength, but also have a high toughness. For examples, the aligned nanofiber mats based on rigid homo-PI (BPDA/PDA) has a tensile strength of 660 MPa and modulus of 15 GPa, much higher than other kinds polymer nanofiber mats,[20] while the 6F-BAPP/BPDA based homo-polyimide nanofiber membrane had a tensile strength of 308 MPa and a toughness of 365 MPa due to the flexible PI molecular backbone.[18] In this study, a series of blend-PI nanofiber membranes were prepared to investigate the effect of moiety of the rigid and flexible components on the mechanical properties. The typical stress-strain curves of the nanofiber membranes were shown in **Fig. 3**, and the corresponding mechanical properties were summarized in **Table 1**. The mechanical properties of blend-PI showed similar trend to that of co-PI with the same monomers and could be tuned by changing the molar ratio of the rigid component (B-PI) and the flexible component (O-PI).[19] As expected, the increased molar ratio of flexible components led to the increase of elongation from 2.59% to 27.08% and the decrease of modulus from 12.12 to 2.54 GPa. As the molar ratio of rigid B-PI decreased, the tensile strength of the blend-PI nanofibers first

increase and then decreased. At the 4/6 molar ratio of B-PI and O-PI, the blend-PI nanofiber membranes showed the highest tensile strength of 1299 MPa and a Young's modulus of 7.68 GPa with an elongation at break of 16.03%. Compared to the nanofiber membranes of rigid B-PI with high modulus and the flexible O-PI with high elongation, the blend-PI nanofibers (at 4/6 molar ratio of B-PI and O-PI) not only possessed a high strength but also a high elongation.
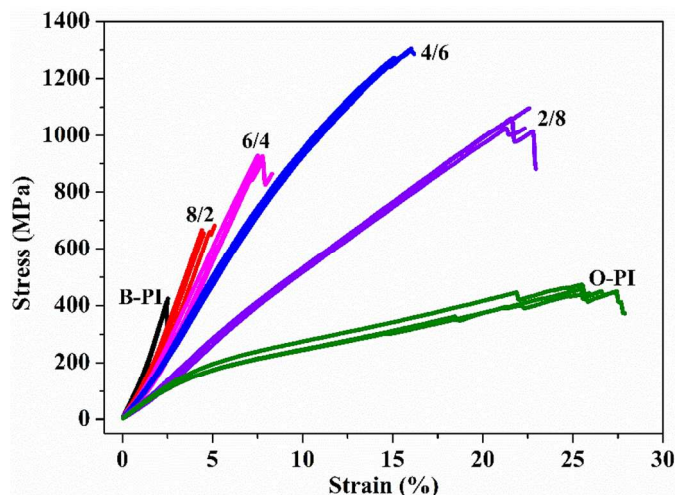
Figure 3. Typical stress-strain curves homo- and blend-PI nanofiber membranes with different molar ratio of B-PI and O-PI.

Table 1. Mechanical properties of electrospun homo- and blend-PI nanofiber membranes.

Molar ratio (B-PI/O-PI)	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)	Toughness (J/g)
100/0(B-PI)	415.64	2.59	12.12	3.34
80/20	668.17	4.68	10.77	9.86
60/40	919.44	7.84	8.31	24.53
40/60	1299.43	15.80	7.68	81.79
20/80	1061.95	22.62	5.50	94.25
0/100(O-PI)	458.26	27.08	3.54	57.62

Toughness is an important parameter to assess the flexibility of materials. The toughness was defined by dividing the integral area under the stress-strain curves by the densities of materials.[27-32] Therefore, the toughness was depending on both the tensile strength and elongation at break. The toughness of material could be greatly enhanced by introducing carbon nanotubes (CNTs), electrospun nanofibers or ultra-flexible materials such as thermoplastic polyurethane (TPU). Blond et al. reported that the toughness of single walled CNTs reinforced polyvinyl alcohol (PVA) electrospun non-wovens was 16 J/g, nearly 7 times that of the PVA film (2.5 J/g).[27] When incorporating TPU into polystyrene (PS) by coaxial and triaxial electrospinning, the toughness of the single coaxial and triaxial composite fibers was 18.6 J/g and 274.5 J/g, respectively, much higher than that of pure PS single fiber (0.4 J/g).[28] Electrospun nylon-6 nanofiber mat had toughness of 21.8 J/g.[29] It was used to enhance the toughness of the brittle melamine-formaldehyde (MF).[29] The nylon-6 nanofibers reinforced MF composites showed toughness in the range of 3.6-27 J/g. A synergistic effect on toughness was observed when using nylon-6 nanofiber to reinforce TPU.[31] The nylon-6/TPU composite

exhibited much higher toughness in the range of 152-274 J/g[30] than pure TPU (111 J/g)[31] and nylon-6 nanofiber mat (21.8 J/g).[29] In this study, the toughness of the blend PI nanofiber membranes could be tuned by change the molar ratio of rigid and flexible moieties. The homo B-PI exhibited toughness of 3.34 J/g while O-PI 57.62 J/g, which was 60% higher than that of PI/MWCNTs composites (0.5-5 vol% MWCNTs, 36 J/g).[32] When increasing the molar ratio of O-PI and B-PI to 6/4 and 8/2, the toughness of the blend-PI increased to 81.79 and 94.25 J/g respectively, only 26% and 15% smaller than the toughness of the well-known ultra-flexible TPU (111 J/g).[31]
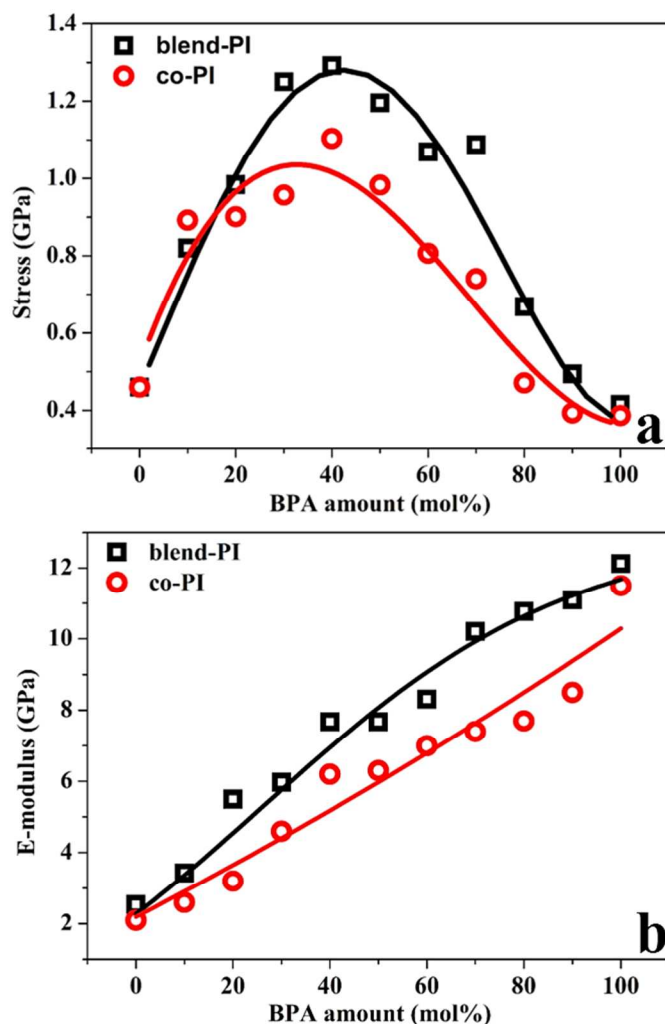

Figure 4. Effect of BPA amount (mol%) on the tensile strength (a) and modulus (b) of blend-PI and co-PI nanofiber membranes.

In our previous report, the mechanical properties of co-PI could be controlled by modifying the molar ratio of monomer diamine BPA and ODA. And the highest tensile strength of 1.1 GPa was obtained at the 4/6 molar ratio of BPA and ODA.[19] **Fig. 4** showed a comparison between tensile strength and modulus of blend-PI and co-PI nanofiber membranes with different amount of BPA (mol %). Both the blend-PI and co-PI nanofibers exhibited the same trend on tensile strength and modulus depending on the amount of BPA and had higher strength than that of homo-PI. The strength of co-polyimide and blend-polyimide increased first and then decreased, while the modulus always kept increase with increasing the ratio of BPA. However, slight difference of tensile strength and modulus

between blend-PI and co-PI was observed from **Fig. 4**. Blend-PI nanofibers showed higher tensile strength and modulus than that of the corresponding co-PI. The highest strength of blend-PI is 1.29 GPa, a little higher than the 1.1 GPa[19] of the co-PI at 4/6 molar ratio of BPA/ODA.
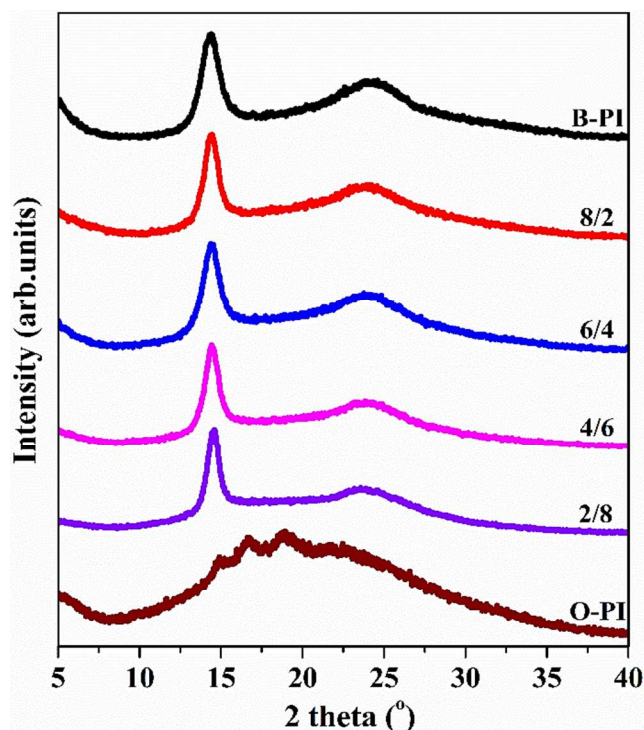

Figure 5. Wide-angle X-ray diffraction (XRD) patterns of the B-PI, O-PI and blend-PI nanofiber membranes with different molar ratios of B-PI/O-PI.

The excellent mechanical properties of co-PI were attributed to the flexible and rigid microblock ordered regions in the nanofibers.[19] However, the reason for the extraordinary mechanical properties of binary blend was much more complicated. The blend-PI was prepared from two kinds of polyamic acids (B-PAA and O-PAA) and the intrinsic viscosities of B-PAA and O-PAA were 5.2 dL/g and 5.8 dL/g respectively. This super-high viscosity of PAA means an ultra-high molecular weight, which guaranteed the high performance of the nanofibers.[16] During the blending of the two PAAs, there were re-equilibration and recombination of different molecular fragments,[33] which might result in the similar molecular structure to the co-PAA, which would be imidized into co-PI. Another explanation of the excellent mechanical properties of blend-PI could be due to the special superstructures. Zhang et al. demonstrated that the space around the paracrystalline domains or between the paracrystalline lamellae was filled with the amorphous segments of the blend-PI based on the studies of wide- and small-angle X-ray and dynamic mechanical analysis of blend-PI film.[34] **Fig. 5** showed the wide-angle X-ray diffraction (XRD) patterns of the O-PI, B-PI and blend-PI nanofiber membranes. Three weak diffraction peaks were observed at about 14.26°, 16.22° and 18.60° for the flexible O-PI nanofiber membranes, indicating the small-partially crystalline. Both the rigid B-PI and blend-PI nanofiber membranes showed a strong diffraction peak at 14.26° and a middle strong peak at 23.94°, implying the existence of paracrystalline domains. No new lattice parameters or new structure information

was found from the X-ray patterns of blend-PI (**Fig. 5**). Based on the recombination phenomenon of the blend-PAAs[33] and the molecular alignment along nanofiber axis during electrospinning,[15] we believe that there are microblock structures, interlamellar and interfibrillar segregations of B-PI in the blend nanofibers (**Fig. 6**).[35] These structures were distributed uniformly along the nanofibers and introduced strong intermolecular interaction, i.e. the state of aggregation of the polymer chains via charge-transfer complex formation.[36,37] Therefore, the blend nanofibers exhibited not only high strength, but also high toughness. Moreover, these multiple superstructures could also be used to explain the higher tensile strength and modulus of blend-PI than co-PI nanofibers with only microblock structures.
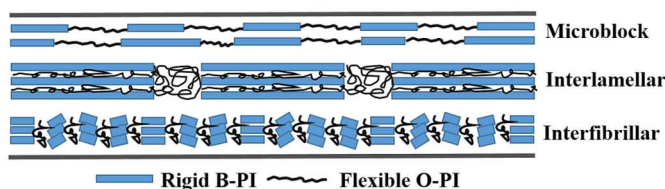

Figure 6. Schematic representation of the microstructure of blend-PI nanofiber with rigid and flexible components.

3.3. Thermal properties and miscibility of blend-PI nanofiber membranes

It is well-known that aromatic polyimides have outstanding thermal stability. **Fig. 7** showed the TGA curves and **Table 2** summarized the thermal properties of pure B-PI, O-PI and blend-PI nanofiber membranes. All the samples showed a high thermal stability of more than 500 °C due to the aromatic backbones. As expected, the thermal stability of the blend-PI nanofiber membranes fluctuated between that of O-PI and B-PI nanofiber membranes. The B-PI backbone was composed of benzene ring structures and imide ring structures. The molecules of this kind of rigid-rod-like polyimide (B-PI) possessed high temperature resistance performance. Compared with B-PI, the flexible -O- ether groups on the O-PI reduced the rigidity of the backbone and made the polymer decompose at a lower temperature. Therefore, as the molar ratio of BPA/ODA increased, the 5% weight loss temperature ($T_{5\%}$) increased gradually from 530 to 587 °C and the decomposed temperature (T_d) increased from 482 to 535 °C because of the inherent oxidation from the increased amount of -O- ether group.
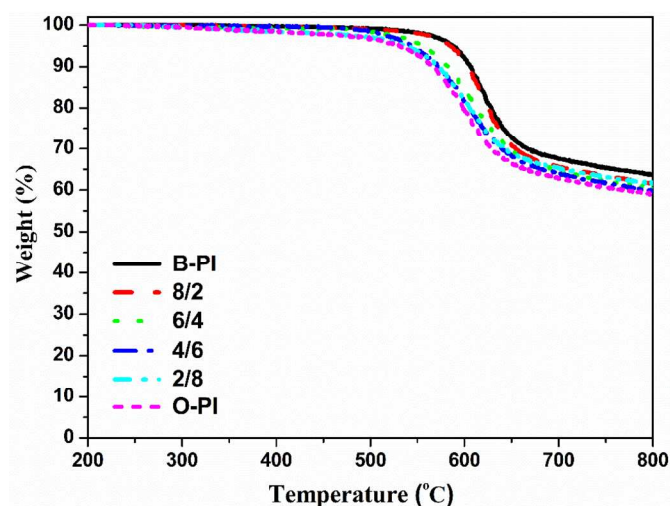

Figure 7. TGA curves of B-PI, O-PI and Blend-PI nanofiber membranes.

Compared to the differential scanning calorimetry (DSC), the dynamic mechanical analysis (DMA) is an effective and sensitive method to determine the glass transition temperature (T_g) of polymers with rigid-rod like molecular chains. The DMA curves (Tan δ) of B-PI, O-PI and blend-PI nanofibers were shown **Fig. 8** and the corresponding T_g was listed in **Table 2**. The flexible O-PI nanofiber membranes showed a prominent α transition peak at 275 °C, which is usually associated with the relaxation of the main backbone chain. As increasing the amount of B-PI, there were more rigid components in the blend and more energy was needed for the movement of molecular chains. Therefore, an increase of T_g and a decrease of Tan δ intensity were observed. When higher molar ratio of the B-PI was applied, e.g. 8/2, almost no α transition could be observed. In this case, the motion of molecules was restricted by rigid component in polymer blend system. However, a medium strong and broad β transition was found from the tan δ curves, which could be attributed to the secondary transition of the movement of aromatic moieties on the backbones.

Table 2. Thermal properties of electrospun PI nanofiber membranes.

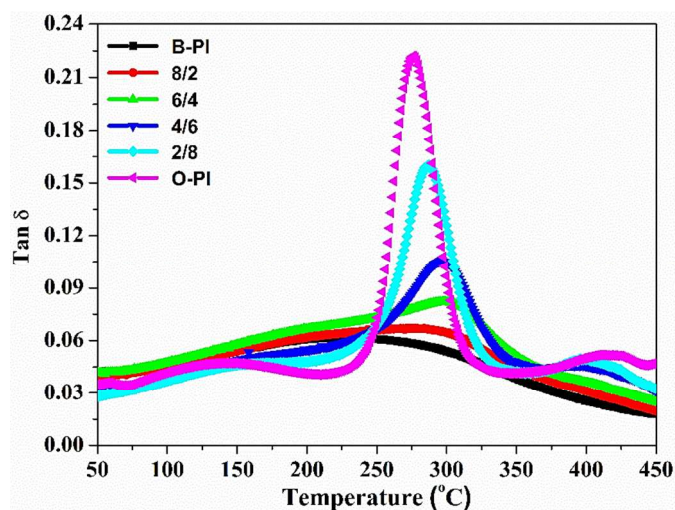| Molar ratio (BPA/ODA)	$T_{5\%}$ (°C)	T_d (°C)	T_g (°C)
0/100 (O-PI)	530	482	275
2/8	536	506	287
4/6	545	508	296
6/4	555	513	299
8/2	584	532	-
100/0 (B-PI)	587	535	-

Figure 8. Tan δ of electrospun B-PI, O-PI and blend-PI nanofiber membranes.

Compatibility or miscibility of the two components is important to the excellent physical properties of the blend. One feasible way to check the miscibility of the blend is to measure the glass transition temperature (T_g) by DSC or DMA. Generally, due to the absence of molecular interactions between the two components, the immiscible blend would show two glass transition temperatures, which come from the respective component.[28] However, the miscible blend

usually showed only one glass transition temperature due to the strong molecular interactions between the chains of each component.[8, 36] In this study, the blend-PI nanofibers showed only one glass transition temperature (**Table 2** and **Fig. 8**), which suggested the good miscibility of the blend-PI due to the strong intermolecular charge-transfer interaction between B-PI and O-PI molecules.

4. Conclusions

High strength and high toughness PI nanofibers were prepared by electrospinning the binary blend of polyamic acids followed with thermal imidization process. The thermal and mechanical properties can be controlled by changing the molar ratio of rigid B-PI component and flexible O-PI component. The glass transition temperature and decomposition temperature of the blend-PI increase gradually with the increased amount of B-PI. The blend-PI nanofibers possess better mechanical properties than the corresponding co-PI. When the molar ratio of B-PI/O-PI is 4/6, the blend-PI has the highest tensile strength of up to 1.3 GPa, which is 200 MPa higher than the corresponding co-PI and nearly 3 times that of homo- O-PI and B-PI. The blend-PI nanofibers with B-PI/O-PI molar ratio of 4/6 and 2/8 show high toughness in the same level of 82 J/g and 94 J/g, respectively, slightly smaller than that of the well-known ultra-flexible thermoplastic polyurethane (111 J/g). All the blend-PI nanofibers exhibited complete miscibility over the whole range of composition. These excellent properties of blend-PI nanofibers are probably attributed to the multiple superstructures and the strong intermolecular charge-transfer interaction between B-PI and O-PI molecules. This blend method of making blend-PI is very simple and can be greatly extended to modify the properties of PIs. Such high strength and high toughness of the blend-PI nanofibers with excellent thermal stabilities promise particular applications in the field of high-temperature composites.

Acknowledgements

Notes and references

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